LOW-DENSITY IONIZATION BEHAVIOR

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1. INTRODUCTION

As part of a continuing study of the physics of matter under extreme conditions, I give some results on matter at extremely low density. In particular I compare a quantum mechanical calculation of the pressure for atomic hydrogen with the corresponding pressure given by Thomas-Fermi theory. (This calculation differs from the "confined atom" approximation in a physically significant way.) Since Thomas-Fermi theory, in some sense, represents the case of infinite nuclear charge, these cases should represent extremes. Comparison is also made with Saha theory, which considers ionization from a chemical point of view, but is weak on excited-state effects. In this theory, the pressure undergoes rapid variation as electron ionization levels are passed. This effect is in contrast to the smooth behavior of the Thomas-Fermi theory. The point of this study is to clarify this theoretical discrepancy. Since for fixed temperature, complete ionization occurs in the low density limit, I study the case where the temperature goes appropriately to zero with the density. Although considerable modification is required, Saha theory is closer to the actual results for this case than is Thomas-Fermi theory.

2. LOW DENSITY BEHAVIOR IN THE THOMAS-FERMI MODEL

As remarked above, the Thomas-Fermi model is, in some sense a model of the limit of an infinite number of infinitesimally charged electrons, and so is the opposite extreme from the Hydrogen atom. Next I give briefly the fundamental equations of the finite temperature, Thomas-Fermi statistical theory of the atom [1-4]. First the electron density is given by

$$\rho(r) = \int_0^\infty \frac{2 \cdot 4\pi p^2 \, dp/h^3}{\exp[\{p^2/(2m) - eV(r)\}/kT + \eta] + 1},$$ (2.1)

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where $-eV(r)$ is the potential energy. Let us define,

$$I_n(\eta) = \int_0^\infty \frac{y^n\, dy}{e^{y-\eta}+1}. \tag{2.2}$$

Then we can use Poisson's equation to determine $V(r)$,

$$\frac{1}{r}\frac{d^2}{dr^2}[rV(r)] = \frac{16\pi^2}{h^3}e(2mkT)^{\frac{3}{2}}I_{\frac{1}{2}}\left(\frac{eV(r)}{kT}-\eta\right). \tag{2.3}$$

The usual reduction of these equations to dimensionless variables [2] uses,

$$c = \left(\frac{h^3}{32\pi^2 e^2 m(2mkT)^{\frac{1}{2}}}\right)^{\frac{1}{2}} \propto T^{-\frac{1}{4}}. \tag{2.4}$$

Let $s = r/c$. Then (2.3) becomes,

$$\frac{d^2\beta}{ds^2} = sI_{\frac{1}{2}}\left(\frac{\beta}{s}\right), \tag{2.5}$$

where

$$\frac{\beta}{s} = \frac{eV(r)}{kT} - \eta, \tag{2.6}$$

since η is independent of r. As $r \to 0$, we must have $V(r) \to Ze/r$ to reproduce the nuclear charge. Therefore as one of the boundary conditions for (2.6), we must have,

$$\beta(0) = \alpha = \frac{Ze^2}{kTc} \propto T^{-\frac{3}{4}}. \tag{2.7}$$

In order to insure that the total number of electrons is Z for a neutral atom inside a sphere whose volume is the average volume per atom, Ω/N, a little manipulation shows that [3],

$$\frac{d\beta}{ds} = \frac{\beta}{s} \text{ at } s = b, \tag{2.8}$$

where $b = r_b/c$. It is useful to introduce the notation,

$$\frac{4\pi}{3}r_b^3 = \frac{\Omega}{N}, \quad x = \left(\frac{128Z}{9\pi^2}\right)^{\frac{1}{3}}\frac{me^2 r_b}{\hbar^2}, \quad \zeta = \frac{ZN}{2\Omega}\left(\frac{h^2}{2\pi mkT}\right)^{\frac{3}{2}}. \tag{2.9}$$

It is convenient now to re-express the Thomas-Fermi equations in terms of my chosen independent variables, ζ and x. To this end let us make the further change of variables

$$s = \sigma b, \quad \beta = \gamma\alpha. \tag{2.10}$$

The defining equations (2.6-8) now become,

$$\frac{d^2\gamma}{d\sigma^2} = \frac{6\sigma}{\zeta\sqrt{\pi}}I_{\frac{1}{2}}\left(\left(\frac{\sqrt{\pi}}{4}\zeta\right)^{\frac{2}{3}}\frac{x\gamma}{\sigma}\right),$$

$$\gamma(0) = 1.0, \tag{2.11}$$

$$\frac{d\gamma}{d\sigma} = \frac{\gamma}{\sigma} \text{ at } \sigma = 1.0.$$

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The goal of this section is to study the behavior as the density goes to zero $(x \to \infty)$, while the deBroglie density, ζ remains fixed.

Our first step is to approximate

$$I_{\frac{1}{2}}(t) \approx \begin{array}{ll} \frac{2}{3}\left(t + 1.10113\right)^{\frac{3}{2}} & t \geq -1.0113 \\ 0 & t < -1.0113 \end{array} \tag{2.12}$$

The rational for this approximation is that it is asymptotically correct for $t \to \infty$ and gives the correct value of $I_{\frac{1}{2}}(0)$. The identity $I_{z-1}(0) = \Gamma(z)\zeta(z)(1 - 2^{1-z})$ allows us to deduce the value of $I_{\frac{1}{2}}(0)$ from the tabulated values of the Riemann ζ-function and the result $\Gamma(\frac{3}{2}) = \sqrt{\pi}/2$. Thus, using this approximation, we can write from (2.11),

$$\frac{d^2\gamma}{d\sigma^2} = \frac{4\sigma}{\zeta\sqrt{\pi}} \left[x\gamma + 1.0113 \left(\frac{\sqrt{\pi}}{4}\zeta \right)^{-\frac{2}{3}} \sigma \right]^{\frac{3}{2}} \tag{2.13}$$

This form suggests the change of variables, $\eta = \sigma/x$ and

$$\Gamma(\sigma) = \gamma(\sigma) + 1.0113 \frac{\sigma}{x\left(\frac{\sqrt{\pi}}{4}\zeta\right)^{\frac{2}{3}}}. \tag{2.14}$$

The defining equations then become,

$$\frac{d^2\Gamma}{d\eta^2} = \eta^{-\frac{1}{2}}\Gamma^{\frac{3}{2}},$$
$$\Gamma(0) = 1.0, \tag{2.15}$$
$$\frac{d\Gamma}{d\eta} = \left.\frac{\Gamma(\eta)}{\eta}\right|_{\eta=x},$$

But these are exactly the same equations which have been studied [4] in connection with the zero-temperature limit of the Thomas-Fermi theory. The solution is,

$$\Gamma(\eta) \approx \left(1 + a\eta^{a_-} + b\eta^{2a_-}\right)^{-1/(2a_-)} \left[1 + \left(\frac{\eta}{144^{1/3}}\right)^{-a_-}\right]^{-a_+/2}, \tag{2.16}$$

where

$$a_- = -0.77200187, \quad a_+ = 7.77200187, \quad a = 1.539233, \quad b = 1.06595. \tag{2.17}$$

In the limit of large x, we get asymptotically,

$$\gamma(\sigma) \asymp \frac{287.40}{x^3\sigma^3} - \frac{1.0113\sigma}{x\left(\frac{\sqrt{\pi}}{4}\zeta\right)^{\frac{2}{3}}} \tag{2.18}$$

It is to be noticed that for small σ, $\gamma(\sigma) > 0$ and for large σ it changes sign. We know the result [5],

$$\frac{Z_i}{Z} = -\sigma_0\gamma'(\sigma_0), \quad \text{where} \quad \gamma(\sigma_0) = 0, \tag{2.19}$$

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where Z_i is the amount of ionization, and we may solve for σ_0 from (2.18). When we note that for small values of Z_i/Z, that

$$\frac{P\Omega}{ZNkT} \approx \frac{Z_i}{Z}, \tag{2.20}$$

then we may compute through a little manipulation, that the pressure is given by

$$P \approx 4907.5 Z^{\frac{10}{3}} x^{-10} \left(\frac{\sqrt{x}}{\zeta^{\frac{1}{6}}} \right)^7 \left[1 + \frac{5.1154}{x^{0.77200187}} \left(\frac{\sqrt{x}}{\zeta^{\frac{1}{6}}} \right)^{0.77800187} + \cdots \right], \tag{2.21}$$

for ζ fixed as $x \to \infty$. Note that the numbers may not be quite right owing to the approximation used for $I_{\frac{1}{2}}(t)$. It is to be noted however, that the leading order powers are as deduced previously by numerical fits. [5]

3. A CELLULAR MODEL OF A DILUTE GAS

In this section I provide motivation and define the model of a gas which I will employ. As rigorously-correct, quantum mechanical models of a gas not available, I shall propose a model which seems physically reasonable to me. Bloch's theorem on crystal lattices [6] says that any solution for the "one-electron wave function" is of the form $\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\phi(\vec{r})$, where $\phi(\vec{r})$ has the periodicity of the lattice. By using all the $\vec{k}$ which lie in the first Brillouin zone, one can construct the entire band corresponding to that state. Since I am mainly concerned here with the case of a very dilute gas, I have basically a "tight binding" situation with a very narrow eigenvalue band associated with each single electron state. Even though I do not have a crystal, such a construction should give a relatively reasonable result for this case. The point is not to construct a band theory of a dilute gas, but rather to use this method to include, at least approximately, the Pauli exclusion principle effects between electrons on different atoms. Exchange effects between them are ignored and are hopefully small in a dilute gas. I will next divide space up into Wigner-Seitz cells. Here the boundary conditions are

$$\psi(\vec{r}) = e^{-i\vec{k}\cdot\vec{R}}\psi(\vec{r} + \vec{R}) \tag{3.1}$$

and

$$\vec{n}(\vec{r})\cdot\vec{\nabla}\psi(\vec{r}) = -e^{-i\vec{k}\cdot\vec{R}}\vec{n}(\vec{r}+\vec{R})\cdot\vec{\nabla}\psi(\vec{r}+\vec{R}), \quad \text{or} \quad \vec{n}(\vec{r})\cdot\vec{\nabla}\phi(\vec{r}) = -\vec{n}(\vec{r}+\vec{R})\cdot\vec{\nabla}\phi(\vec{r}+\vec{R}), \tag{3.2}$$

where $\vec{n}(\vec{r})$ is the normal vector to the surface of the cell and $\vec{R}$ is a lattice vector. These conditions provide for the continuity of the wave function and its derivative at the surface of the cell. We make the approximation that the cell is spherical, which is on the average true because there is no preferred direction in a gas. We add that, to the extent that shape fluctuations are important, they are ignored in this procedure. Using the standard spherical harmonic expansion,

$$\phi(\vec{r}) = \sum_{l,m} Y_{lm}(\theta, \varphi) u_l(r), \tag{3.3}$$

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we find that (3.1) requires the equality of $\phi(\vec{r})$ at the antipodes, and that this condition, coupled with (3.2) requires that for l even the radial derivative of the partial wave function vanishes at the surface and for l odd the partial wave function vanishes at the surface. In the current treatment, we use the same treatment for the odd l as that derived for the even l, because in the low density limit, we expect that this change in boundary conditions will make only a very slight change in the eigenvalues.

In the usual tight-binding approximation, the spread of the eigenvalue spectrum for the many-atom system is calculated in terms of overlap integrals and crystal corrections to the atomic potential. These features are not well defined in this approach, however without being too specific, in order to obtain the spread of eigenvalue spectrum for the many-atom system, we substitute $e^{i\vec{k}\cdot\vec{r}}\phi_\lambda(\vec{r})$ into the Schrödinger equation. It yields, if $\mathcal{H}_0$ is the original Hamiltonian,

$$\frac{\hbar^2 k^2}{2m}\phi_\lambda(\vec{r}) - \frac{i\hbar^2}{m}\vec{k}\cdot\vec{\nabla}\phi_\lambda(\vec{r}) + \mathcal{H}_0\phi_\lambda(\vec{r}) = E_\lambda(\vec{k})\phi_\lambda(\vec{r}) \tag{3.4}$$

There are two terms on the left-hand side of this equation which are explicitly $\vec{k}$ dependent. We note that the parity of $\vec{\nabla}$ is odd, and by the restrictions on the basic wave function mentioned above as imposed by the boundary conditions, the basic eigenfunctions are of fixed parity. Thus if we compute any diagonal matrix element, under the transformation $\vec{r} \to -\vec{r}$ on the integration variable, that matrix element goes into its negative and so vanishes. Thus as all diagonal matrix elements vanish, there will be no first order terms in k (except in degenerate cases). Thus we can conclude that if the $E_\lambda(0)$ are the eigenvalues of $\mathcal{H}_0\phi_\lambda = E_\lambda(0)\phi$, then the eigenvalues are just $E_\lambda(\vec{k}) \approx E_\lambda(0) + \alpha_\lambda\hbar^2 k^2/2m$ for $\vec{k}$ in the spherical approximation to the first Brillouin zone, $|\vec{k}| \le \sqrt[3]{32/\pi}\, me^2/(\hbar^2 x)$. α_λ is an appropriate "band index" dependent quantity to take account of band narrowing. (It is also conceivable because the electron has two spin-states that if the energy difference between the parallel and anti-parallel spin states on adjacent atoms is relatively large, then matters would be more complex.) The scheme in this approach consists of putting a nucleus in the center of a sphere and solving for the radial part of the wave function with the condition that its derivative vanish on the boundary. This model differs from the confined atom of Graboske, Harwood and Rodgers [7-8] in that they require the wave function to vanish on the surface.

Next we need the pressure of an atom enclosed in a sphere at low density and temperature. For simplicity, and practicality, we will treat Hydrogen. We will suppose that the proton is fixed in the center of the sphere. The basic formulas are [9],

$$N = \sum_k \frac{1}{\exp[(\epsilon_k - \mu)/kT] + 1}, \tag{3.5}$$

where here $N = 1$ which fixes μ, as a function of the temperature and the volume. The energy is given by

$$U = \sum_k \frac{\epsilon_k}{\exp[(\epsilon_k - \mu)/kT] + 1}, \tag{3.6}$$

and the grand partition function adds μN to the Helmholtz free energy of the canonical ensemble,

$$A = -\left\{ kT \sum_k \log\left[1 + \exp\left((\mu - \epsilon_k)/kT\right)\right] - \mu N \right\} \tag{3.7}$$

By thermodynamics, the pressure is given by,

$$p = -\left.\frac{\partial A}{\partial \Omega}\right|_T = \sum_k \frac{\left.\frac{\partial \mu}{\partial \Omega}\right|_T - \left.\frac{\partial \epsilon_k}{\partial \Omega}\right|_T}{\exp[(\epsilon_k - \mu)/kT] + 1} - N\left.\frac{\partial \mu}{\partial \Omega}\right|_T,$$

$$= -\sum_k \frac{\left.\frac{\partial \epsilon_k}{\partial \Omega}\right|_T}{\exp[(\epsilon_k - \mu)/kT] + 1}. \tag{3.8}$$

By the notation of (2.9) we can write,

$$p\Omega = -\frac{1}{3}\sum_k \frac{r_b \left.\frac{\partial \epsilon_k}{\partial r_b}\right|_T}{\exp[(\epsilon_k - \mu)/kT] + 1}. \tag{3.9}$$

It is convenient to re-express $\partial \epsilon_k / \partial r_b$ in terms of the wave function. The Schrödinger equation for the radial component of the wave function, is

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}(r\psi_k) - \frac{l(l+1)}{r^2}\psi_k\right) - \frac{e^2}{r}\psi_k = \epsilon_k\psi_k, \tag{3.10}$$

where m is the reduced mass of the electron, with the boundary conditions,

$$\psi_k(0) = \text{finite}, \quad \psi_k'(r_b) = 0. \tag{3.11}$$

With the usual substitution, $r\psi_k(r) = u_k(r)$, the equation (3.10) and the boundary conditions (3.11) become,

$$-\frac{\hbar^2}{2m}\left(\frac{d^2 u_k}{dr^2} - \frac{l(l+1)}{r^2}u_k\right) - \frac{e^2}{r}u_k = \epsilon_k u_k, \quad u_k(0) = 0, \quad u_k'(r_b) = \frac{u_k(r_b)}{r_b}. \tag{3.12}$$

This latter boundary condition is reminiscent of (2.11) in Thomas-Fermi theory. If we take the partial derivative of (3.12) with respect to r_b, $(\frac{\partial u_k}{\partial r_b}|_r \equiv \dot{u}_k)$ multiply by u_k, and integrate with respect to r from 0 to r_b we get,

$$0 = \int_0^{r_b} dr \left[-\frac{\hbar^2}{2m}\left(\frac{d^2 \dot{u}_k}{dr^2} - \frac{l(l+1)}{r^2}\dot{u}_k\right)u_k - \frac{e^2}{r}\dot{u}_k u_k - \frac{\partial \epsilon_k}{\partial r_b}u_k^2 - \epsilon_k \dot{u}_k u_k\right]. \tag{3.13}$$

If we integrate the first term by parts twice and use the Schrödinger equation to show the coefficient of $\dot{u}_k$ vanishes, we get the relation,

$$0 = -\frac{\hbar^2}{2m} \left[\frac{d\dot{u}_k(r_b)}{dr} u_k(r_b) - \dot{u}_k(r_b) \frac{u_k(r_b)}{r_b} + \dot{u}_k(0) u_k'(0) - \frac{d\dot{u}_k(0)}{dr} u_k(0) \right]$$
$$- \frac{\partial \epsilon_k}{\partial r_b} \int_0^{r_b} u_k^2 \, dr. \quad (3.14)$$

The terms evaluated at origin vanish as $u_k(0) = \dot{u}_k(0) = 0$. By wave function normalization, we may rewrite (3.14) as,

$$\frac{\partial \epsilon_k}{\partial r_b} = -\frac{\hbar^2}{2m} u_k(r_b) \left[\frac{\partial^2 u_k(r, r_b)}{\partial r \partial r_b} \bigg|_{r=r_b} - \frac{1}{r_b} \frac{\partial u_k(r, r_b)}{\partial r_b} \bigg|_{r=r_b} \right], \quad (3.15)$$

where I have expanded the notation for $u_k(r) \to u_k(r, r_b)$ for clarity.

We may re-express (3.15) in a more convenient form. To do this we differentiate the boundary condition (3.12) with respect to r_b.

$$0 = \frac{d}{dr_b} \left[r_b \frac{\partial u(r_b, r_b)}{\partial r} - u(r_b, r_b) \right] = r_b \frac{\partial^2 u(r_b, r_b)}{\partial^2 r} + r_b \frac{\partial^2 u(r_b, r_b)}{\partial r_b \partial r} - \frac{\partial u(r_b, r_b)}{\partial r_b}.$$
$$(3.16)$$

With this result we may rewrite (3.15) as

$$\frac{\partial \epsilon_k}{\partial r_b} = \frac{\hbar^2}{2m} u(r_b) \left[\frac{\partial^2 u(r)}{\partial r^2} \right]_{r=r_b}. \quad (3.17)$$

This result has the semi-classical interpretation that it is just proportional to the radial part of the pressure $(\vec{v} \cdot \vec{p})$ on the surface of the enclosing sphere. If we use the Schrödinger equation to eliminate the second derivative, and substitute into (3.9),

$$p\Omega = \frac{1}{3} \sum_k \frac{\left[r_b \epsilon_k + e^2 - \hbar^2 l(l+1)/(2mr_b) \right] [u_k(r_b)]^2}{\exp[(\epsilon_k - \mu)/kT] + 1}. \quad (3.18)$$

The next step is to separate the energy due to the integration over the $\vec{k}$'s from the sum over the discrete states from the solution of Schrödinger's equation in a sphere. For (3.5) we write,

$$N = \int d\vec{k} \sum_\lambda \frac{1}{\exp[(\epsilon_\lambda + \alpha_\lambda \hbar^2 |\vec{k}|^2/2m - \mu)/kT] + 1}. \quad (3.19)$$

Now by Rolle's theorem there exists a value of $|\vec{k}|^2$ such that the result in (3.19) can be obtain by substituting that value in the integrand and multiplying by $\int d\vec{k}$. However, this integral is normalized in such a way as to leave one state per cell. Thus since μ is adjusted in such a way as to give N, the value of μ just changes so as to absorb this value of $|\vec{k}|^2$, and so we need not consider it here. However, in (3.18) we do need to take account of the spread in the energy due to many-electron effects. It

is usual in the "tight binding" approximation to have a factor of the overlap integral in the width of the energy "band." This quantity is not defined in my approach. Consequently, I use a semi-classical argument to select the amount to be inserted. Namely, starting from (3.17), which I treat as $u^* \partial^2 u / \partial r^2$, I multiply u by $\exp(i\vec{k} \cdot \vec{r})$ and find an extra term $|u|^2 \hbar^2 |\vec{k}|^2 / (6m)$. The term linear in $\vec{k}$ vanishes when averaged over the directions of $\vec{k}$ in our spherical approximation. I then approximate the value to insert by the usual linear average, which is $\frac{3}{5}$ the maximum value. This value is appropriate for narrow bands where the weight function of the states changes very little over the width of the band. Likewise, it is appropriate for the bulk of the states for high compressions (not our current interest) and moderate temperatures as again the weight function is relatively constant. In fact in this region, this "band energy" term is the main contribution to the pressure. Thus our expression for the pressure becomes,

$$ p\Omega = \frac{1}{3} \sum_\lambda \frac{\left[\epsilon_\lambda + 3(9\pi/4)^{\frac{2}{3}} \hbar^2 / (10 m r_b^2) + e^2/r_b - \hbar^2 l(l+1)/(2m r_b^2) \right] r_b [u_\lambda(r_b)]^2}{\exp[(\epsilon_\lambda - \mu)/kT] + 1}. $$

(3.20)

Note is taken that for non-compressed systems at low temperatures, the pressure given by this formula can be negative instead of positive. As pointed out by Wigner and Seitz [10], this model can predict cohesive energy, and so there is a meta-stable branch for which $\partial \epsilon / \partial r_b$ can have a positive value instead of a thermodynamically stable negative value.

Further note is taken that when these equations are applied to the ideal gas, the lowest eigenfunction is linear in r. Although this term contributes nothing to the pressure, as $\epsilon_\lambda = 0$, when we use our rule to include the "band energy" additions to the pressure, the factor $r_b u(r_b)^2 = 3$, instead of the proper value 2 for these additions. Fortunately this effect is significant only for $\zeta > 10^{-2}$, and so should not effect our low-density study.

4. NUMERICAL SOLUTIONS AND A COMPARISON

I draw to the reader's attention that, except for the harmonic oscillator problem, the free electron gas, and the Hubbard model for small systems, *etc.*, there are hardly any direct computations of the partition function in the field of quantum statistical mechanics. It is this computation which is required to evaluate the expression for the pressure (3.20). Since there are an infinite number of terms in the sum, we will truncate it by ignoring energy states of suitably high energy which will contribute only a very small amount to the total. The second thing to mention is that as we will treat spin-$\frac{1}{2}$ electrons so there is an overall factor of two to be included in addition to the factor of $2l + 1$ to count the number of m states. The next project is to solve the Schrödinger equation with boundary conditions (3.12) for the eigenvalues, ϵ_k and the the value of the normalized eigenfunctions at the surface $u_k(r_b)$. To obtain this solution, we use the standard difference approximation,

$$ \frac{d^2 u(r)}{dr^2} \approx \frac{u(r+dr) - 2u(r) + u(r-dr)}{(dr)^2}. $$

(4.1)

This procedure leads to a tridiagonal, linear matrix equation to represent the Schrö-dinger equation. The boundary condition at $r = 0$ is accommodated easily by setting $u(0) = 0$. For the boundary condition at $r = r_b$ we wish to maintain the tridiagonal character of the equation matrix. The difference version of this boundary condition becomes,

$$\frac{u(r_{N+1}) - u(r_N)}{dr} = \frac{u(r_{N+1})}{r_{N+1}} = \frac{u(r_{N+1})}{(N+1)dr}, \tag{4.2}$$

which yields directly the result

$$u(r_{N+1}) = \frac{N+1}{N} u(r_N). \tag{4.3}$$

Now by the adjustment of the last diagonal element of the matrix, we can impose the remaining boundary condition while retaining the tridiagonal character of the matrix equations. In order to obtain the eigenvalues and eigenvectors of the difference approximation to Schrödinger's equations, we use the `tqli` subroutine, as modified for double precision, of Press *et al.* [11] The vast bulk of the computational time is consumed by the three lines of code which compute the eigenvectors. Something like the equivalent of 300 hours of Sparc20 time have been used on this project. Note is made that at the end of this project, a small programming error was detected. Spot checks indicate that it does not seem to effect significantly the conclusions.

The next issue is the mesh size and the number of values of l that are required. To insure the the minimum of the potential for the maximum value L of l, is outside the cellular model sphere, we require the condition,

$$L \geq \tfrac{1}{2} \left(\sqrt{1 + 3.54x} - 1 \right) + 10, \tag{4.4}$$

where the 10 is just for safety. In order to assure the the ignored values of l would have made a relatively small contribution, I have selected the rule that the minimum acceptable value of the potential at the surface divided by kT should be 15, which leads a reduction in the relative term-size of the order of 10^6. This rule leads to the requirement,

$$L \geq \sqrt{x + 0.3x^2 T_{\mathrm{maximum}}}, \tag{4.5}$$

where T is in electron volts and T_{maximum} is the largest T used for a particular density. For the mesh spacing, we have required that that the number of steps be the greater of $16x$ or $2xT_{\mathrm{maximum}}$. The first rule reproduces the lowest eigenvalue within five parts in 10^4 in a sphere of radius $x = 8.18$ and the deviation from that for an infinite sized sphere is in the positive direction, as it should be. The second rule is meant to take account of the rate of spatial variation for states with an energy of the order of kT. In our calculations we have used a maximum of 1300 for the number of spatial mesh points and a maximum of 360 for the maximum value of l.

Once the energy eigenvalues and the surface wave functions have been computed, the next step is to solve (3.19) for the free energy, μ. I have solved that equation by a binary search procedure, and have required that (3.19) hold to within one part in 10^{10}. With the value of the free energy, we have all the ingredients necessary to evaluate the pressure, (3.20). Using the normal density of Hydrogen (liquid) as 0.07098 gm/cc, and a gram molecular weight of 1.00797, I have computed the cellular model pressure
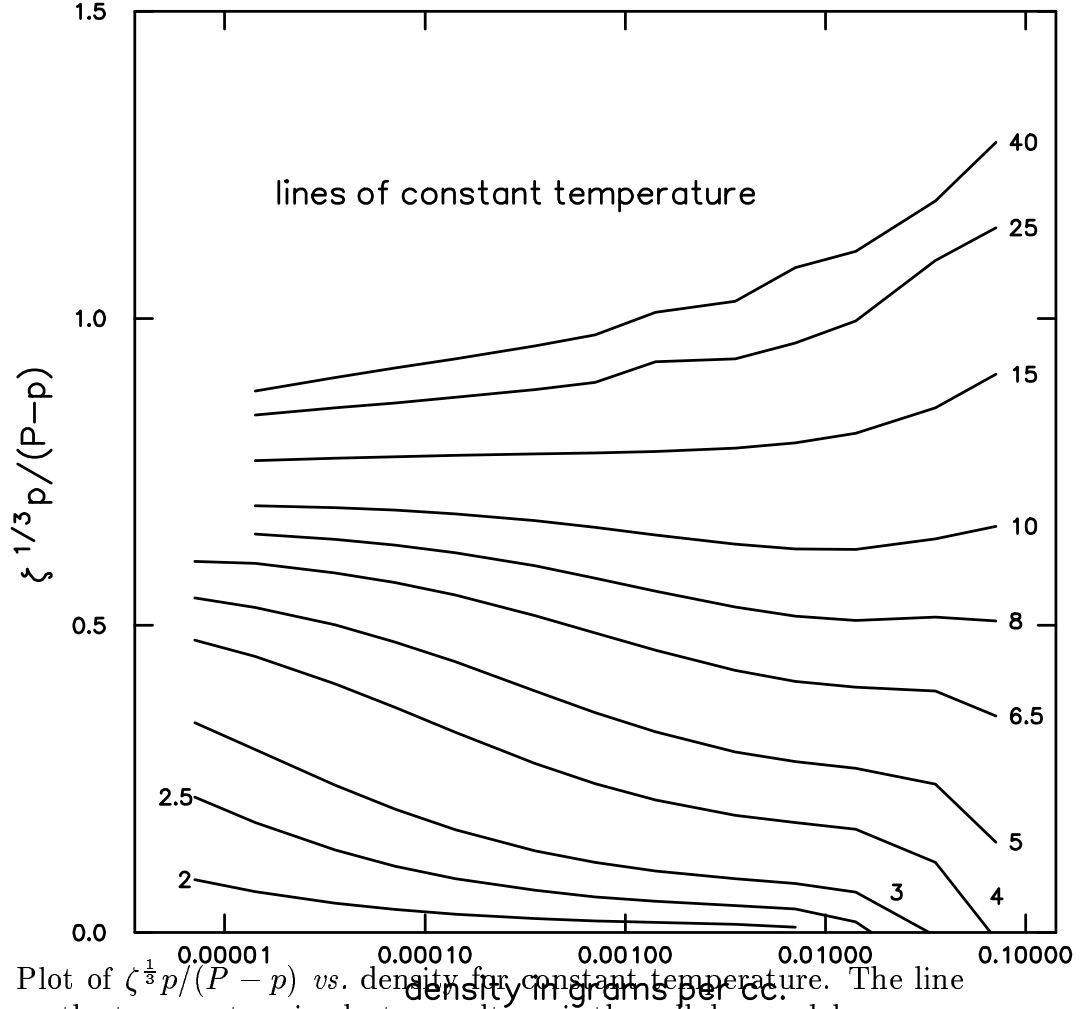
Fig.1. Plot of $\zeta^{\frac{1}{3}} p/(P - p)$ *vs.* density for constant temperature. The line labels are the temperature in electron volts. p is the cellular model pressure and P is the ideal Fermi gas pressure. ζ is given by (2.9).

for compressions from unity to 10^{-4}, which leads to a value of $x = 81.8$ at the lowest compression. I have investigated temperatures of 0.1 to 10^4 electron volts, although I consider only progressively lower temperatures as I study lower compressions, since the temperature at which complete ionization occurs drops as the compression drops.

The Saha ionization formula [12] is

$$\frac{Z_i}{1 - Z_i} = C\zeta^{-1} \exp\left[-\frac{\chi}{T}\right], \tag{4.6}$$

where Z_i is the ionization per atom, and $\chi \approx 13.5978\text{ev}$ is the ionization potential of Hydrogen. This equation suggests that a useful quantity to consider is $Z_i/(1 - Z_i)$. This quantity is almost exactly equal to $p/(P - p)$ where P is the ideal Fermi gas pressure, and p is the pressure in the cellular model. To make a useful figure, it is convenient it turns out, to multiply by $\zeta^{\frac{1}{3}}$, rather than the expected ζ. We display some of our results in Fig. 1. The waver observed at high temperature is due to some numerical inaccuracy and the use of linear interpolation is evident in places. On the
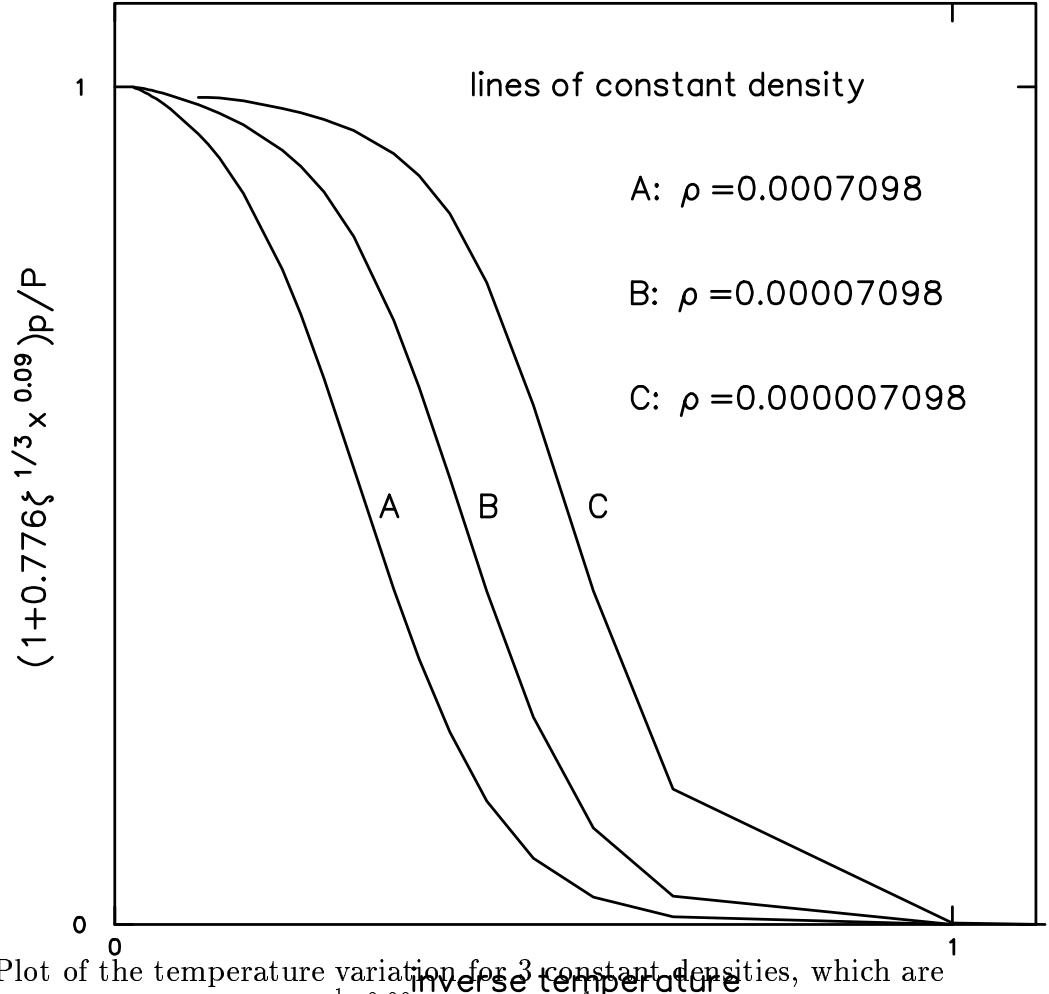
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Fig.2. Plot of the temperature variation for 3 constant densities, which are labeled in gm/cc, of $(1+0.776\zeta^{\frac{1}{3}}x^{0.09})p/P$ $vs.$ T^{-1}, with T in electron volts. p is the cellular model pressure and P is the ideal Fermi gas pressure. ζ and x are given by (2.9).

right (normal density) side of the figure we see at lower temperatures the effects, mentioned earlier, of the cohesive energy predicted by the model. The drop of the pressure to zero is a marker in this theory of a phase transition from a gaseous phase to a condensed phase. A detailed examination of these pressure results (and others not displayed) leads to the conclusion that the numbers displayed in Fig. 1 should be multiplied by $0.776x^{0.09}$. When this is done we see a consistent high-temperature limit for the low density results. The observed $\zeta^{\frac{1}{3}}$ behavior may be an anomaly of the model as a similar sort of feature is seen when the model is applied to the ideal Fermi gas. In Fig. 2 we display some curves of constant density. The effects of linear interpolation is evident at low temperatures. The Saha ionization formula (4.6) suggests that we try a fit of the form $A/(1 + Be^{C/T})$. I have tried this form and find that it works quite well. Specifically I find the following representation for

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the low-density pressure results,

$$p = \frac{P}{(1 + 0.776\zeta^{\frac{1}{3}}x^{0.09})(1 + 3.161x^{-1.71}e^{12/T})}, \qquad (4.7)$$

where P is the ideal Fermi gas pressure and is given [4] by

$$P = \frac{196.6889}{x^5\zeta^{\frac{2}{3}}}g(\zeta), \qquad (4.8)$$

with P in megabars and with $g(\zeta)$ represented to within a tenth of a percent by,

$$g(\zeta) \approx \left[\frac{1 + 0.61094880\zeta + 0.12660436\zeta^2 + 0.0091177644\zeta^3}{1 + 0.080618739\zeta}\right]^{\frac{1}{3}}. \qquad (4.8)$$

The argument of the exponential may be recast in terms of x and ζ as $12/T = 0.227x^2\zeta^{\frac{2}{3}}$.

When we consider, for example, the limit for fixed ζ as $x \to \infty$ then it is the case that the ratio of the pressure to the ideal Fermi gas pressure goes exponentially to zero. On the other hand, by (2.21) the Thomas-Fermi theory result for this same quantity is proportional to $x^{-\frac{3}{2}}$, which substantially under estimates the rate of approach to zero. The same contrast occurs in the zero-temperature problem in infinite volume. The Thomas-Fermi density goes to zero like r^{-6}, while in quantum theory the density decays exponentially. I conclude that while Saha theory needs extensive modification to take account of the effects of excited states, it is the better of the two theories in this regime.

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